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Degradation of Microbial Polyesters: A Theoretical Prediction of Molecular Weight and Polydispersity

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Introduction

Microbial polyesters such as poly(3-hydroxybutyrate), P(3HB), and its copolymers with 3-hydroxyvalerate (3HV) and 4-hydroxybutyrate (4HB) degrade relatively easily in the environment, and they draw much attention due to their potential as biodegradable thermoplastics. These microbial polyesters are known to degrade by the enzymatic action of depolymerase, hydrolysis, or thermal degradation. Grassie *et al.*[1] investigated thermal degradation of P(3HB), and Doi and his collaborators[2−5] studied thermal and hydrolytic degradation of P(3HB), P(3HB-*co*-3HV), and P(3HB-*co*-4HB). Doi and co-workers[2,3] claimed that the 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. Lauzier *et al.*[6] studied hydrolytic degradation of P(3HB) under highly acidic conditions and found a linear relationship between the inverse of the number-average degree of polymerization and time. They conclude the degradation occurred via random chain scission.

We attempted to theoretically calculate the change in the number-average molecular weight and the polydispersity of microbial polyesters as they degrade by random chain scission. And experimental data of Doi *et al.*[2,4,5] and Lauzier *et al.*[6] were compared with our theoretical predictions.

Description of the Model

When all the bonds in a given polymer are assumed to degrade with equal probability, the mechanism of the hydrolysis can be written as

$$P_2 + W \rightarrow 2P_1$$

$$P_3 + W \rightarrow P_1 + P_2$$

$$\vdots$$

$$P_n + W \rightarrow P_{n-r} + P_r \quad (r = 1, 2, ..., n - 1) \quad (1)$$
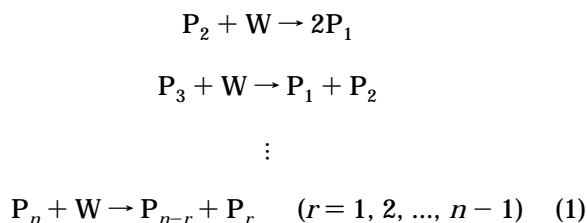
where P_n is the polyester with a number-average degree of polymerization of n and W is a water molecule. If the rate constant of the hydrolysis of each step is k_h, the mole balance equation for each homolog is as follows:

$$d[P_1]/dt = 2k_h[P_2][W] + 2k_h[P_3][W] + ...$$
$$= 2k_h[W]\{[P] - [P_1]\}$$

$$d[P_2]/dt = -k_h[P_2][W] + 2k_h[W]\sum_{i=3}^{\infty}[P_i]$$

$$\vdots$$

$$d[P_n]/dt = -(n-1)k_h[P_n][W] + 2k_h[W]\sum_{i=n+1}^{\infty}[P_i] \quad (2)$$

where $[P] = \sum_{i=1}^{\infty}[P_i]$. When P_2 degrades into P_1, there is only one way that the water molecule can react with the bonds of P_2; however the number of the resulting P_1 is 2. Thus, a factor of 2 is required in eq 2. Also there are two ways that P_n can react with water to produce P_1. On the other hand, since there are $(n - 1)$ bonds in P_n, there are $(n - 1)$ ways for P_n to react with water, and a factor of $(n - 1)$ appears in eq 2.

For nonisothermal reactions τ can be defined by taking the temperature dependence of the rate constant into account:[7]

$$\tau = \int_0^t k_h\{T(t)\}[W]\,dt \quad (3)$$

Then eq 2 becomes

$$d[P_1]/d\tau = 2\{[P] - [P_1]\}$$

$$d[P_2]/d\tau = -[P_2] + 2\sum_{i=3}^{\infty}[P_i]$$

$$\vdots$$

$$d[P_n]/d\tau = -(n-1)[P_n] + 2\sum_{i=n+1}^{\infty}[P_i] \quad (4)$$

Summing all of the individual equations in eq 4,

$$d[P]/d\tau = 2\{[P] - [P_1]\} - \sum_{n=2}^{\infty}(n-1)[P_n] + 2\sum_{n=2}^{\infty}\sum_{i=n+1}^{\infty}[P_i] \quad (5)$$

Since

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

and the moment is

$$\lambda_k = \sum_{n=1}^{\infty}n^k[P_n] \quad (7)$$

eq 5 becomes

$$d\lambda_0/d\tau = (\lambda_1 - \lambda_0)$$

$$\text{at } \tau = 0, \quad \lambda_0 = [P_1]_0 + [P_2]_0 + ...$$
$$= [P]_0 \quad (8)$$

in which $\lambda_1 = \sum_{n=1}^{\infty}n[P_n]$. Since λ_1 is the same as the concentration of the monomer unit, it is considered to

be a constant. Therefore,

$$d\lambda_1/d\tau = 0$$

$$\text{at } \tau = 0, \quad \lambda_1 = \sum_{n=1}^{\infty} n[P_n]_0 = \text{constant} \quad (9)$$

Rearrangement of eq 4 yields

$$d(\sum_{n=1}^{\infty} n^2[P_n])/d\tau = 2 \sum_{n=1}^{\infty} n^2 \sum_{i=n+1}^{\infty} [P_i] - \sum_{n=2}^{\infty} n^2(n-1) [P_n] \quad (10)$$

Using

$$\sum_{n=1}^{\infty} n^2 \sum_{i=n+1}^{\infty} [P_i] = \sum_{n=2}^{\infty} \{(n-1)n(2n-1)\}[P_n]/6 \quad (11)$$

eq 10 becomes

$$\frac{d\lambda_2}{d\tau} = \frac{(\lambda_1 - \lambda_3)}{3} \quad (12)$$

where λ_2 and λ_3 are the second and the third moments, respectively. If the molecular weight distribution is assumed to follow the Schultz−Zimm equation, λ_3 in the right-hand side of eq 12 can be expressed in terms of λ_0, λ_1, and λ_2 as follows:[7]

$$\lambda_3 \cong \lambda_2(2\lambda_2\lambda_0 - \lambda_1^2)/\lambda_1\lambda_0 \quad (13)$$

The number-average degree of polymerization, μ_n is defined as

$$\mu_n = \lambda_1/\lambda_0 \quad (14)$$

When eq 14 is differentiated with respect to τ,

$$\frac{d\mu_n}{d\tau} = \frac{d(\lambda_1/\lambda_0)}{d\tau} = \frac{\lambda_0(d\lambda_1/d\tau) - \lambda_1(d\lambda_0/d\tau)}{\lambda_0^2} \quad (15)$$

Considering that $d\lambda_1/d\tau = 0$,

$$\frac{d\mu_n}{d\tau} = -\mu_n(\mu_n - 1) \cong -\mu_n^2 \quad (16)$$

Integration of eq 16 yields

$$\frac{1}{\mu_n} = \tau + \frac{1}{\mu_{no}} \quad (17)$$

Therefore, a linear relationship between μ_{no}/μ_n and τ is predicted for random chain scission of polymers.

Meanwhile, the weight-average degree of polymerization, μ_w, is expressed as

$$\frac{d\mu_w}{d\tau} = \frac{d}{d\tau}\left(\frac{\lambda_2}{\lambda_1}\right) = \frac{1}{\lambda_1}\frac{d\lambda_2}{d\tau} = \frac{1}{3}\left(1 - \frac{\lambda_3}{\lambda_1}\right) \quad (18)$$

Equation 18 becomes

$$\frac{d\mu_w}{d\tau} = \frac{1}{3}(\mu_w\mu_n - 2\mu_w^2 + 1) \cong \frac{1}{3}(\mu_w\mu_n - 2\mu_w^2) \quad (19)$$
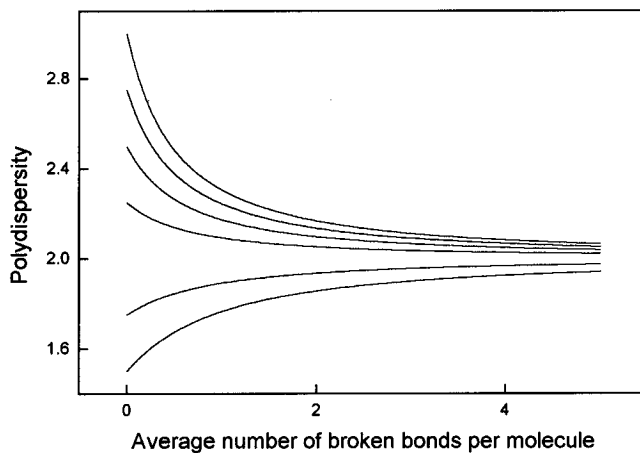

Figure 1. Polydispersity variation due to random chain scission degradation of polymers.

Now, eq 19 can be rearranged into

$$\frac{d\mu_w}{d\tau} - \frac{1}{3}\mu_w\mu_n = -\frac{2}{3}\mu_w^2 \quad (20)$$

A linear differential equation is obtained by using eq 17 as follows:

$$\frac{d}{d\tau}\left(\frac{1}{\mu_w}\right) + \frac{1}{3(\tau + 1/\mu_{no})}\left(\frac{1}{\mu_w}\right) = \frac{2}{3} \quad (21)$$

Equation 21 is then integrated to yield

$$\frac{1}{\mu_w} = \frac{1}{2}\left(\tau + \frac{1}{\mu_{no}}\right) + \left(\frac{1}{\mu_{no}}\right)^{1/3}\left(\frac{1}{\mu_{wo}} - \frac{1}{2\mu_{no}}\right)\left(\tau + \frac{1}{\mu_{no}}\right)^{-1/3} \quad (22)$$

If $\tau \gg 1/\mu_{no}$, then eq 22 can be rearranged to give

$$\frac{\tau^{1/3}}{\mu_w} = \frac{1}{2}\tau^{4/3} + \left(\frac{1}{\mu_{no}}\right)^{1/3}\left(\frac{1}{\mu_{wo}} - \frac{1}{2\mu_{no}}\right) \quad (23)$$

so that a plot of $\tau^{1/3}/\mu_w$ vs $\tau^{4/3}$ should yield a straight line for random chain scission of a polymer having a very high initial number-average degree of polymerization. Ballauff and Wolf[8] also proposed a mathematical model to predict the variation of the molecular weight of polymer molecules. Although their model is very general, it is more implicitly expressed and more complicated so that the deviation of other useful expressions from their model is difficult.

For the case of isothermal degradation of polymes, $\tau = k_h[W]t$ using eq 3 and polydispersity, Q, is a function of time, because

$$Q = \mu_w/\mu_n \quad (24)$$

In general, the number-average molecular weight of the polymer is sensitive to the presence of low molecular weight species, while the weight-average molecular weight is sensitive to the high molecular weight species. Therefore, in order to ascertain that degradation of the polymer is due to random chain scission, it is required not only to demonstrate a linear relationship between $1/\mu_n$ and time but also to show that $1/\mu_w$ or Q behaves according to eq 22 or 24, respectively.
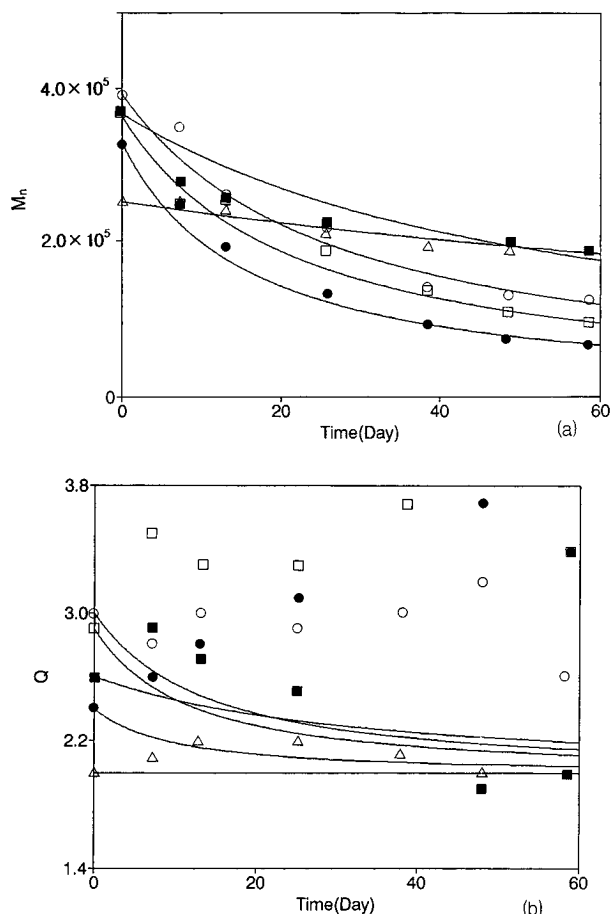
Figure 2. Plots of $\bar{M}_n$ and Q vs time at 55 °C: P(3HB-*co*-45% 3HV) (■); P(3HB-*co*-71% 3HV) (△); P(3HB-*co*-10% 4HB) (○); P(3HB-*co*-17% 4HB) (□); P(3HB-*co*-27% 4HB) (●). Solid lines indicate the calculation based on the data obtained by Doi *et al.*[2]

The average number of broken bonds per molecule, B, is defined as follows:[8]

$$B = \frac{\mu_{no} - \mu_n}{\mu_n} \qquad (25)$$

By combining with eq 17,

$$B = \mu_{no}\tau \qquad (26)$$

Thus, eq 24 becomes

$$Q = \frac{B+1}{\frac{1}{2}(B+1) + \left(\frac{1}{Q_0} - \frac{1}{2}\right)/(B+1)^{1/3}} \qquad (27)$$

It should be noted that the change in polydispersity resulting from random chain scission depends upon the initial polydispersity only and it is independent of the initial molecular weight. Figure 1 shows the polydispersity change as a function of the average number of broken bonds per molecule according to eq 27. The major portion of the polydispersity change occurs during the early stage of the degradation. When B is greater than 3, the change in the polydisperity is expected to be quite small.

According to the random chain scission model

$$\lim_{\tau \to \infty} Q = 2 \qquad (28)$$

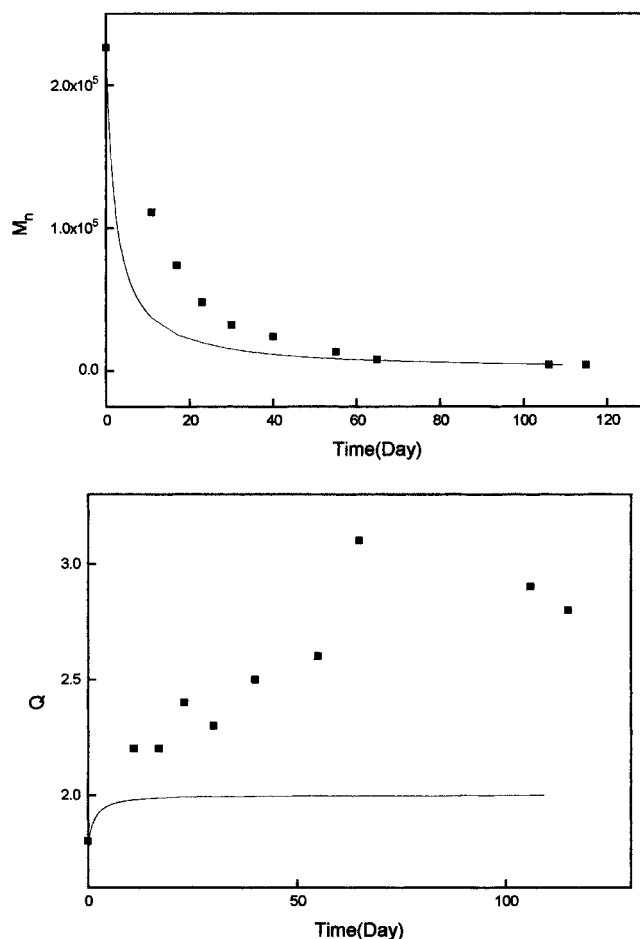which is consistent with the extrapolation of eq 24. It

Figure 3. Plots of $\bar{M}_n$ and Q vs time for P(3HB-*co*-9% 4HB). Data obtained by Doi *et al.*[5]

should be pointed out that eq 28 is valid when both μ_n and μ_w remain much larger than 1, which has been the basis of the derivations so far. However, as polymers degrade to monomeric species completely, Q should approach 1. If the polydispersity index of the initial polymer is less than 2, it will increase up to a value of 2 as random chain scission progresses. 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. Therefore, in order to effectively monitor the mechanism of degradation of microbial polyesters, it would be beneficial to work with polymers with an initial polydispersity index far greater or less than 2.

Degradation of Microbial Polyesters

We applied the analysis result of the random chain scission degradation model to the experimental results of the hydrolytic degradation of microbial polyesters. Since eqs 17 and 22 were derived by assuming μ_n and μ_w were far greater than 1, the concept of the average number of broken bonds per molecule should be used accordingly. The effect of the morphological heterogeneity such as crystallinity of microbial polyesters upon the degradation mechanism can be manifested if the hydrolysis results are compared with the model described in the previous section. In Figure 2 we plotted $\bar{M}_n$ and Q of P(3HB-*co*-3HV) and P(3HB-*co*-4HB) as a function of hydrolysis time at 55 °C, which were experimentally obtained by Doi *et al.*[2] Also shown are the theoretical predictions of $\bar{M}_n$ and Q, based on eqs
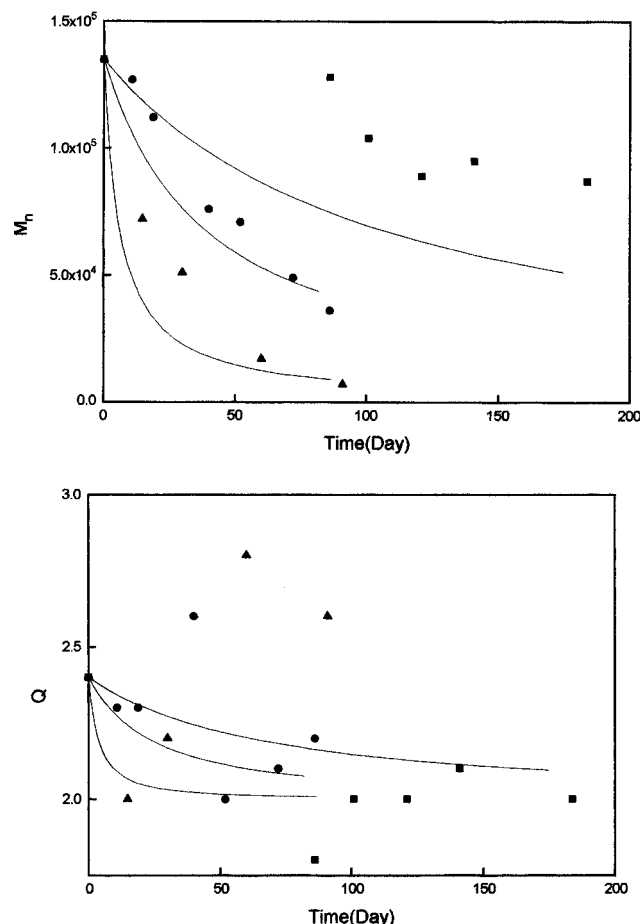
Figure 4. Plots of $\bar{M}_n$ and Q vs time for P(3HB-*co*-14% 3HV). Data obtained by Kanesawa and Doi.[4]

17 and 24, respectively. They determined the rate constant of hydrolysis from the slope of the plot of $1/\mu_n$ vs time. However, the value of the water concentration, [W] should be taken into account in order to utilize eq 17. In fact [W] is the actual concentration of water at the reaction site. However, we used the bulk water concentration for [W], which was calculated by using the water density at the degradation temperature. And, the hydrolysis reaction rate constant was calculated by dividing their rate constant by the water concentration. As shown in Figure 2a, the agreement between the theoretical calculation and the experimental data of Doi *et al.*[2] is fairly good. It is partly because the value of k_h was borrowed from their experimental data. However, the time dependence of the experimentally determined Q is quite different from the prediction of eq 24 (Figure 2b).

Figure 3 shows the change in the number-average molecular weight and polydispersity of P(3HB-*co*-9% 4HB), which was obtained by Doi *et al.*[5] at 70 °C and pH 7.4. While the number-average molecular weight agrees with the prediction of eq 17 based on the random chain scission degradation model, the agreement between the prediction of eq 24 and the experimental result was quite poor. As shown in Figures 2 and 3, P(3HB-*co*-4HB) exhibits a greater discrepancy than P(3HB-*co*-3HV) does. In fact, in P(3HB-*co*-3HV) the charge densities around the carbonyl carbon of HBHB, HBHV, HVHB, and HVHV are expected to be quite similar, regardless of the comonomer sequence, while in P(3HB-*co*-4HB) those of 3HB3HB, 3HB4HB, 4HB3HB, and 4HB4HB would be widely different from each other. Since hydrolysis normally proceeds by the nucleophilic
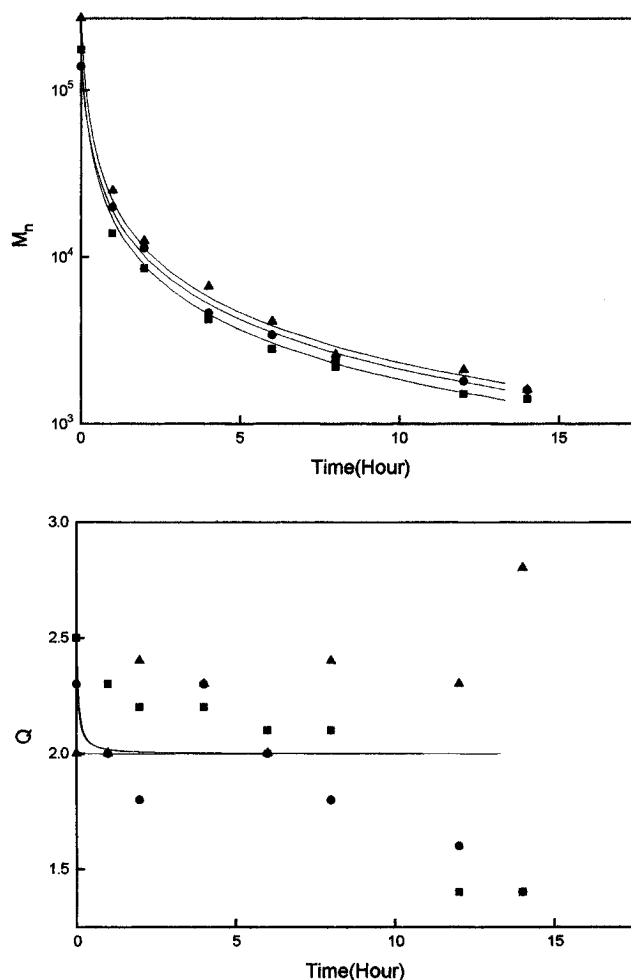

Figure 5. Plots of $\bar{M}_n$ and Q vs time for P(3HB). Data obtained by Lauzier *et al.*[6]

addition of water molecules onto carbonyl carbons, hydrolysis of P(3HB-*co*-4HB) can be regarded to occur preferentially at specific ester linkages rather than to occur at random places with equal probability.

Kanesawa and Doi[4] studied the hydrolytic degradation of P(3HB-*co*-14% 3HV) in an aqueous solution of pH 7.4 at three temperatures. Figure 4 compares their data with the simulation results of $\bar{M}_n$ and Q using the degradation rate constants obtained from the least-squares analysis of the experimental data. Clearly, the random chain scission model does not predict hydrolysis of P(3HB-*co*-14% 3HV) under these conditions. In Figure 5 same comparison is made for hydrolysis of P(3HB) at 104.5 °C in an aqueous solution of 3.0 N HCl, observed by Lauzier *et al.*[6] The number-average molecular weight follows the prediction of the random chain scission model based on eq 17; however, the change in polydispersity deviates greatly from 24. The discrepancy between the experimental data of hydrolytic degradation and the random chain scission model for not only P(3HB-*co*-3HV) but also P(3HB) is partly due to the measurement error of the molecular weight and the molecular weight distribution. The fact that the hydrolysis rate of the crystalline region is different from that of the noncrystalline region is also expected to contribute to the discrepancy. This effect would be particularly pronounced when the hydrolysis is quite fast, as in Figure 5. Hydrolysis may produce water-soluble low molecular weight substances, which may not be appropriately taken into account in determining the molecular weight experimentally.
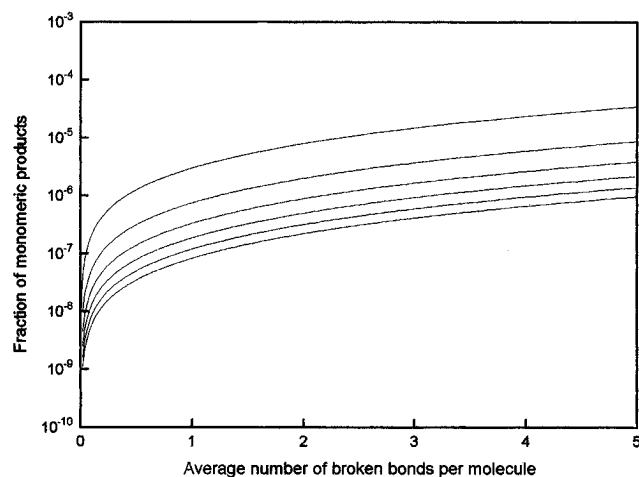
Figure 6. Plots of fraction of monomeric products vs average number of broken bonds.

Combining eqs 4 and 8 yields

$$[P_1] = \lambda_1 - 2(\lambda_1 - \lambda_0|_{\tau=0})e^{-\tau} + (\lambda_1 - 2\lambda_0|_{\tau=0})e^{-2\tau} \quad (29)$$

where the concentration of the monomer at the beginning of hydrolysis, $[P_1]_0$, was assumed to be zero. Equation 29 can be rearranged using eq 26 as

$$\frac{[P_1]}{\lambda_1} = 1 - 2\left(1 - \frac{1}{\mu_{no}}\right)e^{-B/\mu_{no}} + \left(1 - \frac{2}{\mu_{no}}\right)e^{-2B/\mu_{no}} \quad (30)$$

where λ_1 is the total number of monomer units in the sample. Since eq 30 was in principle derived from eqs 17 and 25, which is valid for $\mu_n \gg 1$, it should also be obtained by integrating eq 16 for $\mu_n \rightarrow 1$ and $B \rightarrow \mu_{no} - 1$. Thus

$$\frac{[P_1]}{\lambda_1} = 1 - \frac{2(\mu_n - 1)}{\mu_n} + \frac{\mu_{no} - 2}{\mu_{no}}\left(\frac{\mu_{no}}{\mu_{no} - 1}\right)^2\left(\frac{\mu_n - 1}{\mu_n}\right)^2 \quad (31)$$

If τ becomes ∞, then μ_n approaches 1 and $[P_1]/\lambda_1$ approaches 1. Figure 6 plots the calculation results using eq 30 for various initial number-average degrees of polymerization ranging from 1000 to 6000 with an increment of 1000. The lower the initial number-average degree of polymerization, the faster the rate of increase in the fraction of the monomeric species against the total number of monomeric units in the sample. Doi *et al.*[2] studied P(3HB-*co*-3HV) with the initial degree of polymerization of 2660 until the average number of broken bonds, *B*, reaches 0.96 (Figure 2). In Figure 4 the initial number-average degree of polymerization of P(3HB-*co*-14% 3HV) was 1540 and Kanesawa and Doi[4] ran the hydrolysis until *B* becomes 18. However, Lauzier *et al.*[6] used P(3HB)s with initial number-average degrees of polymerization of 1610, 2020, and 3120, and they found *B* reached 166 at the end of the experiment. Therefore, the formation of water-soluble substances was one of the factors causing the discrepancy between the experimental data and the theoretical calculations.

In conclusion, to confirm that the hydrolytic degradation of P(3HB) and its copolymers occurs via random chain scission, the following must be satisfied (i) hydrolysis proceeds slowly enough that the effect of the nonhomogeneity arising from the crystalline region would be minimized, (ii) the initial number-average molecular weight is large enough, and (iii) the formation of water-soluble substances as a result of hydrolytic degradation would be properly taken into account.

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